

PROGRESS AND FINAL REPORT

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CONTAINING HETEROCYCLIC RADICALS AND
ELECTRICAL INFLUENCES ON NON-RADIATIVE
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**TABILITIES OF NITROGEN CONTAINING HETEROCYCLIC
RADICALS AND GEOMETRICAL INFLUENCES ON
NON-RADIATIVE PROCESSES IN
ORGANIC MOLECULES**

by



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Part I

Stabilities of Nitrogen Containing Heterocyclic Radicals

INTRODUCTION

This report is divided into three essential sections plus a final review section.

Part I Stabilities of Nitrogen Containing Heterocyclic Radicals

Part II Computation of Simple Potential Energy Surfaces for Ground and Excited States

Part III Photophysical Properties of Indolizine

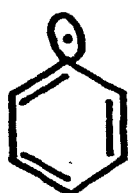
Part IV Final Review of the Accomplishments of Research Done Under This Grant

Part I of this report was carried out in large part at the University of California, Santa Cruz, with some additional calculations done at the Centre de Mecanique Ondulatoire Appliquee in Paris. Part II was carried out in large part using the computing facilities in Paris. Part III was carried out entirely at the University. Drs. Paul Horowitz and Dan Lerner, Messrs. T.S. Lee and G. Feler are acknowledged as coworkers.

INTRODUCTION

This paper addresses itself to three main topics. First we will explore the intuitive ambiguities of attempting to assign the ground state symmetries of a number of heteroradicals. We will also explore the difficulty of obtaining "good" pi-electron spin density calculations. Finally we will also explore the state symmetry consequences of these assignments with respect to the photogeneration of such radicals from parent filled shell molecules.

Conceptual ambiguities exist with respect to intuitively assigning the symmetry of the ground state of planar radicals. Kasai and coworkers¹ set out to explore this issue with respect to the ground state symmetries of the phenyl and higher polycyclic aromatic radicals. Kasai showed¹ that in the systems studied aryl radicals invariably had sigma structures. The simplest resonance structure representation of the sigma phenyl radical is as shown below. The pi-radical is an excited state of the phenyl radical. At this time we will avoid the problem of assigning the proper group theoretical representations for various resonance structures. This would require writing a number of additional structures of proper phasing. In our diagram we use the Salem-Dauben-Turro convention², of circling the sigma electrons and giving the summation of the total number of pi and sigma electrons involved in the critical portion of the bonding picture.



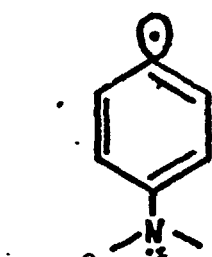
$6\pi, 1\sigma$



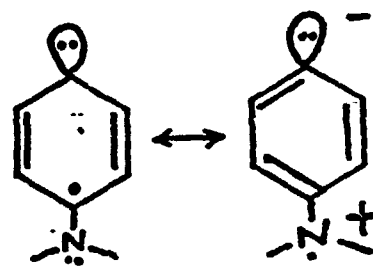
$5\pi, 2\sigma$

Single Structure Representations of the Ground and Excited State of the Phenyl Radical.

Kasai's experimental results were also supported by INDO calculations. Kasai specifically explored the possibility that in electron rich systems the pi-orbitals might yield up an electron to a half-filled sigma orbital to generate a pi-radical. In the case of a substituted phenyl radical the electron donating substituent might stabilize the normally energetically unfavorable zwitterionic resonance structure to yield such a pi-radical, as shown below. INDO calculations,³ however, indicated that the ground state of



$8\pi, 1\sigma$
Sigma Radical



Pi Radical, $7\pi, 2\sigma$

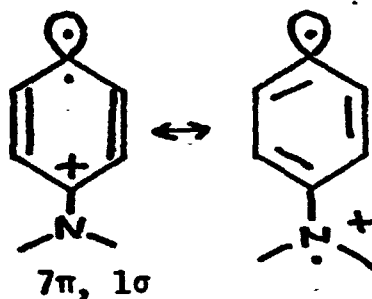
Structure Representations of the Sigma and Pi-p-Aminophenyl Radicals

the p-aminophenyl radical is sigma. We know of no case in which the ground state of aryl radicals are predicted to be pi.

Although not a radical the case of the phenyl cation, an even electron molecule, is somewhat more complex. Experimental information is unclear⁴ as to the existence of the phenyl or substituted phenyl cations in solution. The INDO calculations⁵ predict that although phenyl cation has a sigma structure, the p-aminophenyl cation has a triplet ground state, pi-cationic structure.



$6\pi, 0\sigma$



$7\pi, 1\sigma$

Structure Representations of the Ground States of the Phenyl and p-Aminophenyl Cations

Here, the hypothesis that the electron-rich nature of the substituent could yield an inversion of ground-excited state symmetries has computational support.

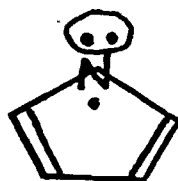
Due to the lack of experimental information this ambiguity as to the real symmetries of the ground state of aryl cations remains. We are attempting to resolve this ambiguity by studying the photoprocesses in arenediazonium salts.

The ambiguity we wish to explore here has to do with the ground state symmetries of radicals generated from the removal of an H atom from R_2N-H yielding R_2N radicals. Because of the nitrogen lone pairs an ambiguity exists as to whether such radicals are pi or sigma. The pyrrolyl radical (I) is a case in point. The sigma and pi-structures of the pyrrolyl radical might be represented as follows. We use the convention of having the pi-electron labeled within the ring.



$6\pi, 1\sigma$

Sigma



$5\pi, 2\sigma$

Pi

Structure Presentations for the Pyrrolyl Radical (I)

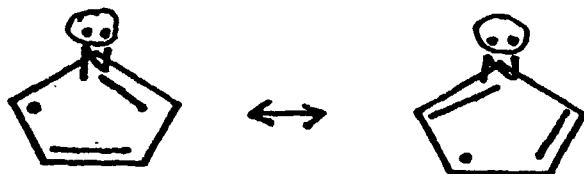
A reasonable guess as to the probable ground state symmetry of the pyrrol radical is obtained from examining the electronic structure of the parent amino radical NH_2 , or simple alkyl derivatives. In the case of NH_2 both experimental⁵ and theoretical⁶ information shows that the ground state has a 2B_1 symmetry, while the lowest excited state 2A_1 is only about 1-3 ev higher in energy.⁷



Structure Representations for the Ground and First Excited State of the Amino Radical

Dialkylamino radicals⁸ are also theoretically and experimentally pi-radicals (2B_1). Simple first order perturbation theory leads an ambiguity as to the prediction of the symmetry of the ground state of the pyrrol radical. The least complicated scheme (Figure 1) of the interaction of the pi-orbitals of cis-butadiene with the pi-amino radical predicts, on weak interaction, a 2B_1 structure for pyrrol, and on strong interaction, a 2A_1 structure. Such a simple picture, however, discounts the possibility that the a_1

sigma orbital on the amino group is stabilized on coalescence into butadiene. In fact, both INDO and pi-electron calculations predict a ground state symmetry of 2A_2 for pyrrolyl (vide infra). Resonance-wise, such a symmetry can only arise from the interaction of structures whose alpha pi-spins are not localized on the nitrogen atom, as shown above, but on the carbon atoms as shown below.



It would appear that simple perturbation arguments are useless in rationalizing the likely ground state symmetries of amino type radicals which have adjacent pi-systems. In a similar way the question as to why NH_2 and NF_2 have 2B_1 ground states and NO_2 has a 2A_1 ground state has not been rationalized. It would appear that predictions as to the symmetries of these classes of molecules can be made only with some computational effort. Hopefully, after a sufficient number of calculations some rationale can be constructed which will aid intuition.

We are particularly interested in the electronic structures of pyrrolyl, imidazyl, and benzimidazyl. Here, we report that INDO calculations predict a sigma structure

for imidazyl, while the other two are pi. Additional calculations were conducted on related heteroradicals to see if the pi-versus-sigma dilemma could be resolved. Finally, we have conducted a number of pi-electron calculations on pyrrol, imidazyl, benzimidazyl, carbazyl, and purinyl radicals.

METHOD OF CALCULATIONS

The INDO calculations were conducted using program No. 91 from Quantum Chemistry Program Exchange.⁹ The standard parameterizations were used.⁶ This program does not compute pure doublet states, however, and thus the results reported here are for calculations containing contaminating higher multiplets. The geometries chosen were those from standard tables⁶ (for N-H and C-H) with the exception that all C-N, C-C, C-O bonds were set at 1.40 Å.

The pi-electron calculations were conducted using a standard open shell UHF pi-electron technique¹⁰ contained in a modified version of program 76 of QCPE. In this case, however, the contaminating quartet multiplet was removed by single annihilation using a subprogram written with the aid of previous work.¹¹ The carbon and nitrogen parameters for the valence state ionization potential and one-centered electron repulsion integral were 11.08, 10.98 eV (carbon) and 14.63 and 12.27 eV (nitrogen) respectively. A test calculation on the allyl radical gave a value of $\langle S^2 \rangle$

after annihilation, of 0.75000, indicating full quartet removal. The calculated terminal and central carbon atom spin densities, after annihilation, were 0.57 and -0.14, using a C-C resonance integral of -2.40 ev. There are in excellent agreement with the experimental values of 0.58 and -.16, respectively.¹²

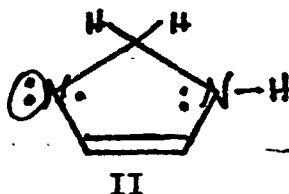
RESULTS AND DISCUSSION

I. INDO Calculations

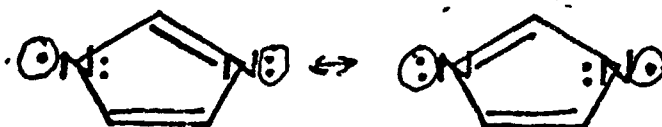
A) Pyrryl, Imidazyl and Benzimidazyl. The calculations listed in Tables 1-3 for these radicals show that both pyrryl and benzimidazyl are predicted to be pi-radicals while imidazyl is predicted to be a sigma radical. Experimentally none of these parent radicals are known. The tetraphenylpyrryl and triphenylimidazyl are well characterized^{13, 14} as being pi-radicals. However, from resonance considerations alone, it would be anticipated that the polyphenyl substituted pyrryl and imidazyl would be pi-radicals even if the parent radicals were sigma. The INDO calculations of pyrryl approximates the pi-electron calculation in that a very low spin density is predicted for the nitrogen atom and that the symmetry is most likely 2A_2 (experimentally) for the tetraphenyl derivative.¹³ Both INDO and pi-electron calculations (Tables 1 and 9, respectively) predict a much higher spin density at the alpha than at the beta nitrogen. Likewise, the triphenylimidazyl shows a low spin density on the nitrogen atoms^{13, 14} although the symmetry predicted from pi-calculation (Table 9) indicates a

2B_1 symmetry, different than pyrrolyl. A rationalization of this will be given later as well as a comparison of the calculations on benzimidazyl presented in Tables 3 and 12.

The main anomaly occurs with the predicted sigma structure of the imidazyl radical. A number of experiments have been directed towards generating the imidazyl and benzimidazyl radicals.¹⁵⁻¹⁷ Imidazyl radical is a proposed intermediate in oxidative phosphorylation, a key biological process.¹⁴ The radical identified from the irradiation of imidazole crystals^{15,17} has been established as being structure II.



The earlier work of Lamotte and Servoz-Gavin^{15a} indicated two different species, one formed at 77K, as yet unidentified, and a higher temperature specie, structure II. A single ESR spectrum indicated a species with 2 equivalent nitrogens with a coupling constant of 10.5 gauss, and one hydrogen atom (32 gauss). The proposed structure^{15a} is close to that of the sigma imidazyl radical (III).



Structure Representation for the Sigma-Imidazyl Radical (III)

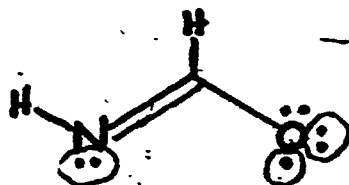
The main problem with such a structural assignment from this sparse data is the low coupling constant on the nitrogen. Most authors¹⁸ associate a low nitrogen coupling constant (under 25 gauss) with a pi-structure, the classical argument being that any sigma radical would have a high s-orbital component and therefore a high coupling constant. The INDO calculation in Table 2 is somewhat unique in that although most of the spin is localized on the two nitrogen atoms the p-orbital, not the s-orbital, component is high. Regardless of the possible relationship of this calculation to reality it is now established that using low coupling constant magnitudes as a criteria of pi-versus-sigma structure has no theoretical validity. Another curious result of the calculation on imidazyl is the generally low value of both the hydrogen and nitrogen coupling constants. In any case the high H coupling constant observed experimentally is not duplicated computationally and no conclusion can be drawn. The ESR spectrum (a single line) for solution generated imidazyl^{16c} indicates rapid spin exchange and is useless for any analysis.

B) Structurally Related Radicals. As previously mentioned, amino and dialkylamino radicals are predicted and found^{6,8} to have pi-structures (2B_1). At present, there is no substantiated case of a sigma radical of the R'RN type. This includes amido,^{18,19} and hydrazido²⁰ type radicals as well as N-alkoxy²¹ radicals. Of major

interest are the amido radicals. A great deal of controversy exists over their structure as determined from ESR spectra.^{18,19} INDO calculations were only reported in detail on a few of the amino type radicals.^{8,18} Possibly²² the acetamido is predicted to be a pi-radical. The main theoretical problem we face here deals with the possible validity of INDO calculations in predicting the relative stabilities of two close lying electronic states. Additional test calculations were conducted in order to explore this situation.

The main question is why is there a pi-to-sigma inversion in going from pyrrolyl to imidazyl? Does it happen in other heteroradicals? Are the calculations reliable? A plausible hypothesis for the pi-to-sigma radical conversion is that the multiple incorporation of heteroatoms having "non-bonding" electrons into a basic hydrocarbon radical might sufficiently electron enrich the sigma framework so as to generate an inversion of the "ground" and "excited" states. Conceptually pyrrolyl and imidazyl are, respectively, aza- and 1,3-diaza cyclopentadienyl radicals. The incorporation of one or more nitrogen atoms into cyclopentadienyl could, conceptually, convert a pi to a sigma radical. Computationally this only occurs with imidazyl. To see if a similar thing occurs when heteroatoms are substituted into a parent allyl radical INDO calculations were carried out on aminoethylene (Table 4), 2-aza-aminoethylene (Table 5), formamido (Table 6),

the formic acid cation (Table 7) and the carboxyl radical (Table 8). The latter three materials were predicted to be sigma radicals. Both aminoethylene and 2-aza-aminoethylene radicals are perturbationally related to the 2A_2 structure of the allyl radical.²³ In contrast with acetamido,²² formamido is predicted to have a sigma structure. As with imidazyl, formamido is predicted to have a curious electronic structure. Most of the spin density is localized on the oxygen atom and the structure representation is closer to that shown below. In addition the nitrogen coupling constant



Structure Representation for the Formamido Sigma Radical

is small. Experimental results on the methylated amido radicals indicate a pi-structure,^{18,19} and thus the experimental results are not necessarily in conflict with the INDO calculations. It is known, from photoelectron spectroscopy,^{24,25} that the formic acid cation is most probably a sigma (n-electron excitation) radical. Here too, the pi-versus-sigma structures are quite sensitive to methylation.²⁵

Carboxyl is predicted to be a sigma radical, and there is some experimental evidence for this²⁶ in the case of malonic acid. However, with phenylcarboxyl radical a

pi-structure is predicted and found.²⁷ Thus, in all cases apparently minor structural variations can cause a pi-to-sigma inversion.

Conclusions of the INDO Calculations. Enough information exists to support the statement that the prediction that imidazyl is a sigma radical is not necessarily a computational artifact. At a minimum the calculations indicate that there is no strong intuitive basis on which to predict what kind of structures should be pi or sigma radicals. However, there is also some support for the idea that loading a particular parent radical with heteroatoms having "non-bonding" electrons should tend to favor sigma structures.

II. Pi-Electron Calculations

The results of the open shell single annihilation SCF pi-electron calculations of the spin and electron densities of pyrrol, imidazyl, indolyl, carbazyl, benzimidazyl, and purinyl radicals are shown in Tables 9-13. Unlike allyl radical,²⁸ it was found that annihilation had little effect on calculated spin and electron densities. Therefore, all the spin and electron densities, as well as the expectation value of S^2 , are reported after annihilation of the contaminating quartet. As usual, there is some ambiguity as to what values to use for the C-C and C-N resonance integrals. Two separate calculations were attempted in all cases. One set of parameters used resonance integrals for C-C and C-N of -2.40 ev each. Another set used a value of -2.40 for C-C and

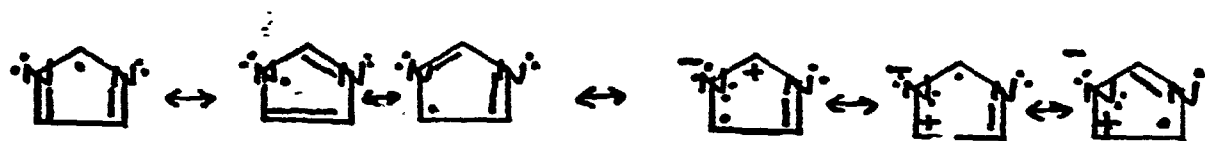
and -2.57 for C-N. In most cases this small parameter change had little effect on the calculated spin and electron densities and, therefore, all the results are not presented. An example of a lack of effect of changing resonance parameters is shown in purinyl (Table 13). With carbazyl, however, a major effect was noted with regard to S^2 , and a minor effect in the spin and electron densities. In one case, benzimidazyl (Table 12), the symmetry of the ground state, was altered by this small change in the resonance integral. Indolyl (Table 10) showed some variation in spin densities.

Two major conclusions can be drawn from the computational features of the calculations presented in Tables 9-13. First, unlike allyl, annihilation is not particularly important in effecting the spin and electron densities. The effect shows up with regard to the expectation value of S^2 , but even in this case single annihilation is not always sufficient in producing a value near the 0.75 required for a pure doublet. Second, the fact that a minor variation in the resonance integral can lead to great changes in spin and electron densities, as well as produce a change in the symmetry of the ground state is a serious development. Such a symmetry change is unlikely for a small system in which there are a limited number of orbitals. In large systems the number of molecular orbitals increases and their close energetic proximity may make the system of interest susceptible to perturbational sensitivity resulting from minor parameter changes. If so, the results

obtained do not reflect topological effects but merely are artifacts of the parameters used.

Without going through a full perturbational treatment of the electronegativity effects of the inclusion of nitrogen atoms into the basic parent hydrocarbon radicals, cyclopentadienyl, indenyl and fluorenyl, the results obtained in Tables 9-13 show some interesting effects. The suppression of the spin density on the N atom in pyrrolyl is due to the 2A_2 symmetry of the radical. This can be re-explained in orbital terminology as resulting from a node through the N-atom in the one electron filled orbital if one uses a closed shell approximation. Under such conditions, the spin density at the N atom would be zero. The situation as to why there is negative spin density in the open shell calculation is identical to the classic case of the allyl radical,²⁸ which also has an 2A_2 symmetry. No such argument can be used with imidazyl and the near zero spin density on the nitrogen atoms must result from electronegativity effects. The simplest hypothesis for imidazyl, or any other radical in which symmetry does not dominate the N spin densities, is that high spin densities and the accumulation of a negative charge on the N atom tend to be mutually incompatible. The reason for this is best seen from resonance structure arguments. Like cyclopentadienyl uncharged resonance structures (of proper phasing and belonging to the 2B_1 representation in the case of imidazyl) merely scatter the spin density equally about the 5 membered ring. However, ionic resonance structures in which

N atoms possess a negative charge suppress the spin densities at the N atom.



non-charged

ionic

Resonance Structure Presentations for the 2B_1 pi-Imidazyl Radical

If this hypothesis is true one would expect to find a correlation between N spin densities and electron densities in the calculations presented in Tables 9-13. In fact, with the exception of the 1 and 3 positions on purinyl radical (Table 13) there is a fair linear correlation. High N spin densities are associated with electron densities in the 1.15 - 1.20 region. Negative spin densities are associated with electron densities in the order of 1.35. Even in purinyl radical the low spin densities of the nitrogen atoms in the 6 member ring is associated with a high electron density. Simply stated, it would seem that nitrogen would prefer to attract 2 electrons instead of one. This fits our intuition as to the relative electronegativities of carbon and nitrogen.

A comparison of the INDO (Table 3) and the pi-electron calculations (Table 12) for the 2A_2 state of

benzimidazolyl radical shows a strong difference in the predicted hyperfine coupling constants. As implied from the pi-electron spin densities the pi-electron calculation shows a fairly high coupling constant for atom 2 in the 6 member ring. The INDO calculations predict very little spin density in the 6 member ring, with the 5 member ring being allyl-like. In particular the lack of annihilation in the case of the INDO calculations shows up in the large negative spin density at carbon 5. This is also shown in the INDO calculations in pyrrolyl (Table 1) and 2-aza-aminoethylene radicals (Table 5). In pi-electron calculations on pyrrolyl we found pi-spin densities of -0.048, 0.418, and 0.106 before annihilation and -0.081, 0.445, and 0.095 after (Table 9) for the nitrogen atom 1 and carbon atoms 2 and 3, respectively. Any presumption that if annihilation is not important in determining spin densities in open shell pi-electron calculations they will also be unimportant in the INDO calculations, is obviously not supported by these results.

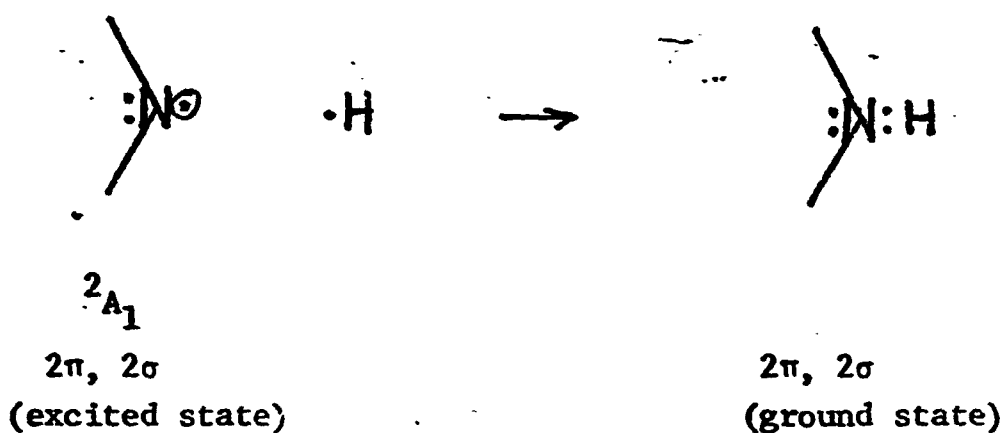
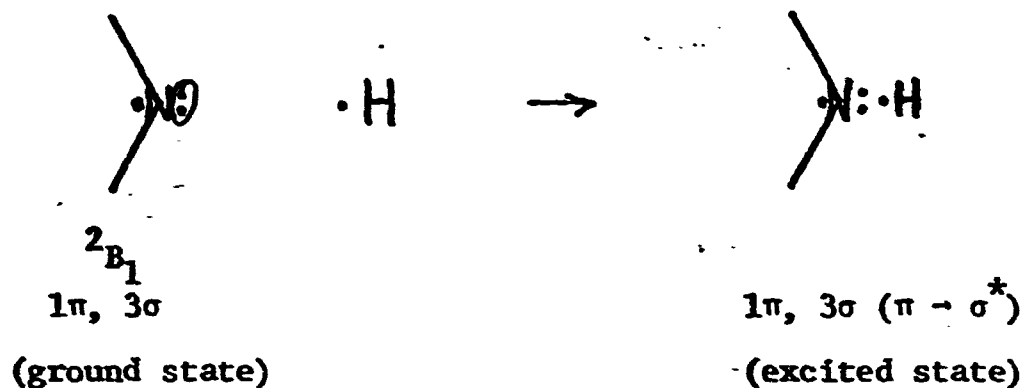
Experimentally, there is a lack of information in which to test these calculations. In the parent hydrocarbon radicals, the ESR spectrum of cyclopentadienyl has been reported.²⁹ In the aza derivatives, only carbazolyl has been characterized.^{1,30} Here, our calculations indicate a nitrogen spin density (0.46) somewhat in excess of the 0.24 estimated from the coupling constant of 6.9 gauss. We are

in qualitative agreement with the observed spectrum, however, and the symmetry of the carbazyl radical must be 2B_1 . The only other material reported is indolyl radical.³¹ The radical is a possible intermediate in the photodecomposition of indole derivatives, including tryptophan. The proposed mechanism³⁰ involves the photo ejection of an electron to give an indole cation followed by ionization to the conjugate base, the indolyl radical. The observed spectrum consists of a single line however.³¹ The argument of Pailthroe and Nicholls that the spin density is localized totally on carbon atom 3 is computationally not supported (Table 10) nor is it logical from a purely resonance viewpoint. The calculation does indicate an unusually high C spin density of 0.50 at the 3 position but the spin densities at the other locations should create significant splitting in the spectrum of indolyl.

III. State Symmetry Consequences of the Pi-Versus-Sigma Structure of Radicals

The symmetries of the ground and excited states of radical species are of importance in determining some of the qualitative features of the potential energies surfaces of even electron molecules which give radical products. This is best seen in how ammonia might yield the amino radical and the hydrogen atom. It has already been shown that the ground state of NH_2 is 2B_1 and the first excited state is 2A_1 .

Conceptually we can join planar NH_2 with H in a coplanar fashion to give planar ammonia. The structure representations are given below.



Structure Representations for the Joining of the ${}^2\text{B}_1$ and ${}^2\text{A}_1$ States of NH_2 Radical with a Hydrogen Atom

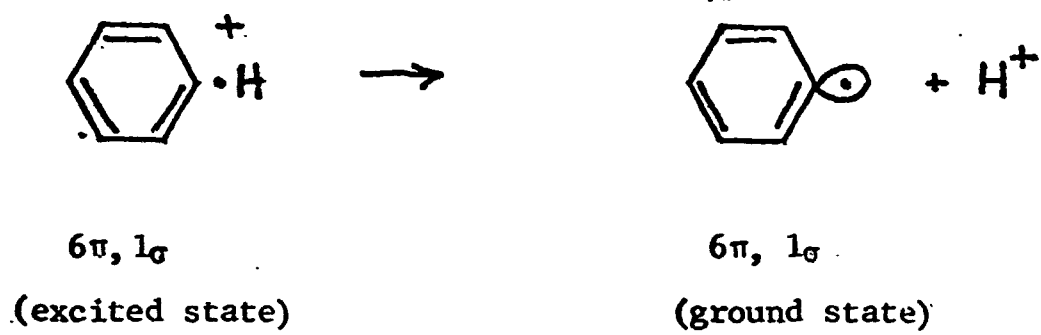
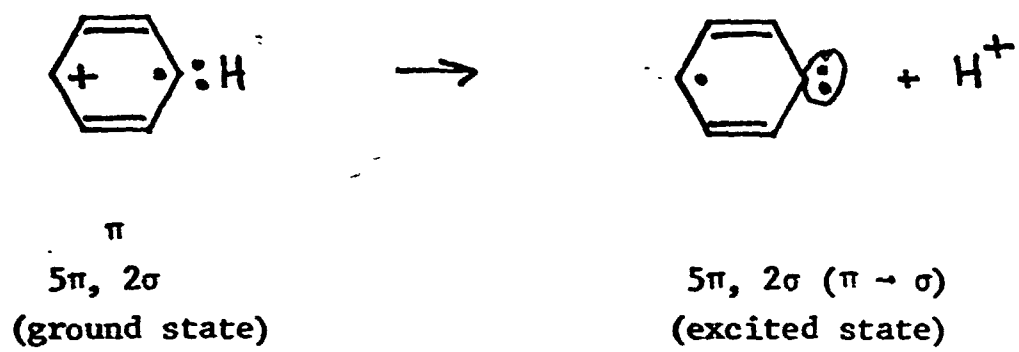
We have purposely written a 3 electron sigma bond for the N-H bond in the ${}^2\text{B}_1$ NH_2 -H reaction. In orbital terminology a 3 electron sigma valence bond is a $(\text{sigma})^2\text{sigma}^*$ configuration. The concept of a 3 electron bond is useful in attempting to keep the state symmetries in order when writing valence bond structures.

The above argument shows that the ground state of the amino radical is correlated with an excited state of ammonia, and the excited state of the amino radical is correlated with the ground state of ammonia. This has already been shown diagrammatically by Herzberg and Douglas.³³ Thus, it is predicted that the potential energy surface of the ground state planar ammonia must cross with a singlet excited state of planar ammonia at a N-H bond length less than the dissociation limit. Because of configuration interaction and the breakdown of symmetry this crossing does not necessarily occur when other geometrical variations are added to the N-H stretch. Conceptually, however, crossing does occur at least at one set of geometrical coordinates.

With the possible exception of imidazyl and foramido, the experimental results show that all other R'RN type radicals are amino-like and yield pi rather than sigma radicals in the ground state. With pyrrole, for example, the stretching of the N-H bond in a co-planar fashion should yield a sigma pyrryl radical, which is predicted to be an excited state of pyrryl. As with amino, then, the ground state of pyrrole is correlated with an excited state of pyrryl (2A_1) and some pi-sigma* excited state of pyrrole is correlated to the ground state of pyrryl (2A_2). It seems likely that in most molecules of the type calculated here, there is a crossing between the ground and excited states at some N-H stretching coordinate.

The behavior of planar heteromolecules having N-H bonds is to be contrasted with the arene-aryl radical correlation curves. The ground state of planar benzene should smoothly give the ground state of the phenyl radical (σ)¹ and an H atom without ground-excited state crossing. A similar analysis will also show that ground-excited state surface crossing is possible in other cases. For instance, the phenoxy radical is known to have a π -structure.³⁴ If one constricts the departure of the H atom from phenol in a coplanar fashion this can only generate a σ phenoxy radical. Thus, as some geometrical coordinate along the O-H stretch the ground and some excited state of phenol come into contact. We have proposed a similar ground-excited state crossing in the thermal and photodecomposition of arene-diazonium cations to give aryl cations.³⁵

Similar ground and excited state curve crossings are proposed for radical cations or anions in their ionization processes. The benzene cation (π)³⁶ can not correlate with the ground state of the phenyl radical (its conjugate acid) which is σ ¹ if the proton departs in a co-planar fashion. Likewise, the ground state of the chlorobenzene anion (presumably a π -radical anion) can not correlate the ground state of the chloride ion and the phenyl radical. Both in the benzene cation and chlorobenzene anion, surface crossing must occur along the breaking of the C-H or C-Cl bond.



Ionization of the Benzene Cation to the Phenyl Radical

The theoretical consequences of these curve crossings are that when attempts are made to calculate the potential surfaces for reactions in which the final states indicate curve crossing the situation will become increasingly complicated as certain bonds are stretched. The experimental consequences of the possibility of ground and excited state relaxation to a ground state potential surface might occur at or near the crossing coordinate. Salem, Dauben and Turro have already² proposed that surface crossing of this type occurs in the singlet Norrish Type II photoreaction. In this case the crossing occurs directly from the $n\text{-}\pi^*$ singlet along the O-H coordinate to give the singlet biradical intermediate in its ground state.

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(b). G. Herzberg, "Advances in Photochemistry", Vol. 5, pp. 3-8, Interscience, N. Y. (1968).
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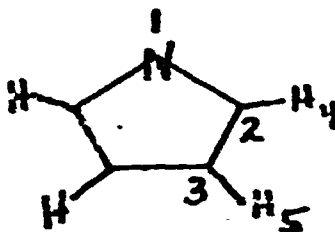
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TABLE 1
Calculated Electronic Structure for the Pyrrol Radical

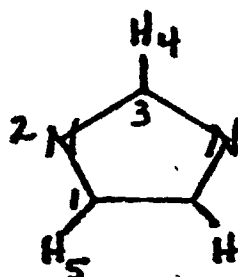


Atom	Orbital*	Electron Densities TOTAL		Spin Densities	Hyperfine Coupling Constant
1	s	1.543		-0.009	- 3
	px + py	2.473	5.299	-0.042	
	p π	1.282		-0.229	
2	s	1.077		0.026	21
	px + py	1.891	3.802	0.032	
	p π	0.834		0.491	
3	s	1.051		0.002	1
	px + py	1.939	4.015	-0.007	
	p π	1.205		0.124	
4	s		1.015	-0.022	-12
5	s		1.020	-0.005	- 3

Symmetry = 2A_2 (π)

* px + py = sum of in plane orbitals

Table 2
Calculated Electronic Structure for the Imidazyl Radical

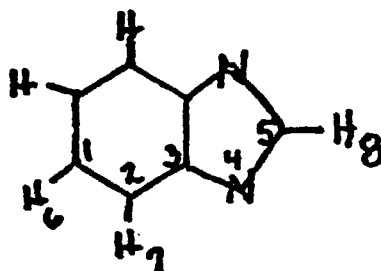


Atom	Orbital	Electron Densities		Spin Densities	Hyperfine Coupling Constant
		TOTAL			
1	s	1.045		0.011	9
	px + py	1.818	3.957	-0.002	
	pπ	1.094		-6.005	
2	s	1.538		0.011	4
	px + py	2.182	5.119	0.091	
	pπ	1.399		0.033	
3	s	1.115		-0.046	-37
	px + py	1.704	3.833	0.028	
	pπ	1.014		-0.056	
4	s		0.996	0.001	0.3
5	s		1.011	-0.002	-1

Symmetry = 2B_2 (sigma)

Table 3

Calculated Electronic Structure of the Benzimidazolyl Radical

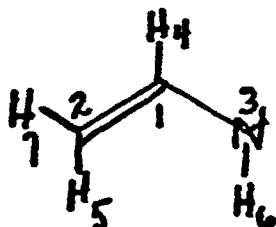


Atom	Orbital	Electron Densities		Spin Densities	Hyperfine Coupling Constants
		TOTAL			
1	s	1.037		0.001	0.5
	px + py	1.939	3.976	-0.001	2
	p π	1.001		0.032	
2	s	1.045		0.003	2
	px + py	1.947	3.985	0.003	
	p π	0.994		0.063	
3	s	1.022		-0.005	-4
	px + py	1.880	3.910	-0.017	
	p π	1.008		-0.018	
4	s	1.550		0.025	10
	px + py	2.631	5.168	0.028	
	p π	0.987		0.621	
5	s	1.079		-0.029	-24
	px + py	1.742	3.841	-0.050	
	p π	1.020		-0.397	
6	s		1.019	-0.002	- 1
7	s		1.019	-0.003	- 2
8	s		1.005	0.014	8

Symmetry = $^2A_2 (\pi)$

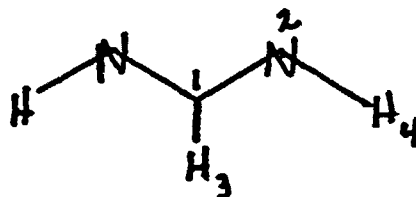
Table 4

Calculated Electronic Structure for the
Aminoethylene Radical (π)



Atom	Orbital	Electron Densities TOTAL		Spin Densities	Hyperfine Coupling Constant
1	s	1.045		-0.022	- 18
	px + py	1.850	3.865	-0.044	
	p π	0.971		-0.290	
2	s	1.102		0.027	22
	px + py	1.936	4.028	0.038	
	p π	0.991		0.494	
3	s	1.564		0.034	13
	px + py	2.604	5.207	0.029	
	p π	1.039		0.796	
4	s		1.014	0.010	6
5	s		0.904	-0.029	-16
6	s		0.988	-0.022	-12
7	s		0.996	-0.022	-12

Table 5
Calculated Electronic Structure for
Aza-amino Ethylene Radical



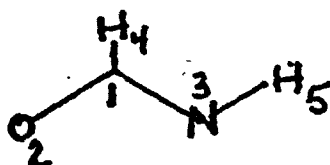
(Cisoid Configuration)					
Atom	Orbital	Electron Densities TOTAL		Spin Densities	Hyperfine Coupling Constants
1	s	1.061		- 0.032	- 26
	px + py	1.757	3.755	- 0.053	
	p π	0.937		- 0.420	
2	s	1.564	—	0.030	11
	px + py	2.604	5.200	0.034	
	p π	1.031		0.710	
3	s		1.056	0.014	7
4	s		0.895	- 0.028	- 15

Symmetry = 2A_2 (π)

Note: Transoid configuration essentially the same with regard to hyperfine coupling constants.

Table 6

Calculated Electronic Structure for the
Foramido Radical (cisoid)*



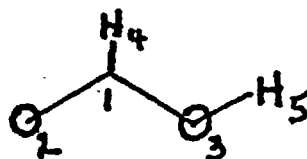
Atom	Orbital	Electron Densities		Spin Densities	Hyperfine Coupling Constant
			TOTAL		
1	s	1.050		-0.027	- 23
	px + py	1.745	3.628	-0.088	
	p π	0.823		0.007	
2	s	1.765		0.019	17
	px + py	2.546	6.104	0.863	
	p π	1.794		0.020	
3	s	1.573		-0.006	- 2
	px + py	2.403	5.360	0.101	
	p π	1.383		-0.027	
4	s		1.003	0.143	76
5	s		0.906	-0.004	- 2

Symmetry = sigma

*Hyperfine coupling constant for isomer with H₄ + H₅ in a trans configuration are: Atom: 1, -24; 2, 16; 3, -7; 4, 49; 5, -7.

Table 7

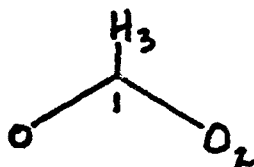
Electronic Structure of the Formic Acid Cation Radical



Atom	Orbital	Electron Densities		Spin Densities	Hyperfine Coupling Constant
			TOTAL		
1	s	1.054		- 0.029	- 24
	px + py	1.731	3.398	- 0.094	
	pπ	0.610		- 0.031	
2	s	1.761		0.021	18
	px + py	2.511	5.880	0.881	
	pπ	1.608		0.042	
3	s	1.638		0.001	1
	px + py	2.737	6.157	0.118	
	pπ	1.782		- 0.011	
4	s		0.877	0.107	58
5	s		0.688	- 0.004	- 2

Symmetry = sigma

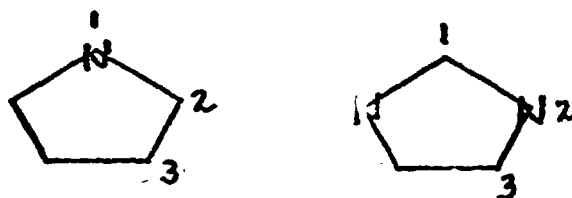
Table 8
Calculated Electronic Structure for the
Carboxyl Radical



Atom	Orbital	Electron Densities		Spin	Hyperfine
			TOTAL	Densities	Coupling Constant
1	s	1.052		- 0.039	- 32
	px + py	1.725	3.484	- 0.092	
	pπ	0.707		- 0.024	
2	s	1.802		- 0.001	- 1
	px + py	2.834	6.283	0.447	
	pπ	1.647		0.012	
3	s		0.950	0.238	129

Symmetry = 2A_1 (sigma)

Table 9
Pi-Spin and Electron Densities of
Pyrrolyl and Imidazyl Radicals

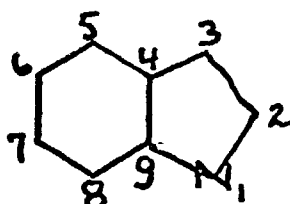


Atom	Spin Density	π -Electron Density
Pyrrolyl		
1	- 0.08	1.37
2	0.45	0.81
3	0.10	1.01
$\langle S^2 \rangle = 0.750$, Sym = 2A_2		
Imidazyl		
1	0.36	0.74
2	- 0.04	1.34
3	0.37	0.79
$\langle S^2 \rangle = 0.756$, Sym = 2B_1		

* All β 's = - 2.4 ev, all values after annihilation.

Table 10

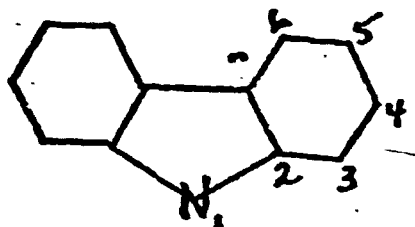
π -Spin and Electron Densities in Indolyl Radical



Atom	Spin Density		Electron Densities	
	All β 's = - 2.4	$\beta_{C=C} = 2.40$ $\beta_{C-N} = - 2.57$	All β 's = - 2.4	$\beta_{C-C} = - 2.40$ $\beta_{C-N} = - 2.57$
1	0.28	0.14	1.25	1.30
2	-0.04	0.06	0.89	0.87
3	0.50	0.49	0.92	0.91
4	-0.07	-0.04	1.06	1.07
5	0.19	0.16	0.97	0.94
6	-0.06	0.02	1.01	1.02
7	0.14	0.10	0.98	0.96
8	-0.02	0.04	0.97	0.97
9	0.08	0.05	0.96	0.95
		$\langle S^2 \rangle =$	0.786	0.750

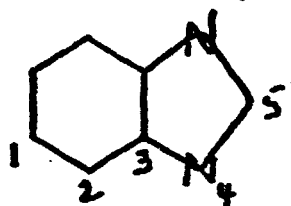
All values after annihilation

Table 11
 π -Electron Spin and Electron Densities
 for Carbazyl Radical



Atom	Spin Densities		Electron Densities	
	All β' 's = -2.40	$\beta_{C-C} = -2.40$ $\beta_{C-N} = -2.57$	All β' 's = -2.40	$\beta_{C-C} = -2.40$ $\beta_{C-N} = -2.57$
1	0.49	0.46	1.17	1.19
2	-0.08	-0.02	0.98	0.97
3	0.19	0.10	0.97	0.96
4	-0.08	-0.02	1.01	1.02
5	0.16	0.11	0.98	0.98
6	-0.06	0.01	0.99	1.00
7	0.12	0.09	0.99	0.99
Sym. = 2B_1		$\langle S^2 \rangle =$	0.906	0.750

Table 12
 π -Spin and Electron Densities for
 Benzimidazyl Radical

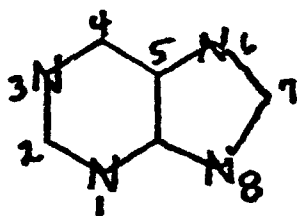


Atom	Spin Densities		Electron Densities	
	All β 's = - 2.4	$\beta_{C-C} = - 2.40$ $\beta_{C-N} = - 2.57$	All β 's = -2.40	$\beta_{C-C} = - 2.40$ $\beta_{C-N} = - 2.57$
1	0.17	0.05	0.94	0.98
2	-0.05	0.20	1.01	0.91
3	0.26	-0.04	0.82	0.99
4	-0.02	0.35	1.38	1.19
5	0.28	-0.11	0.71	0.85
Sym = 2B_1		$^2A_2 \langle S^2 \rangle =$	0.766	0.755

All values after annihilation

Table 13

π -Spin and Electron Densities for
PurinyI Radical



Atom	Spin Densities		Electron Densities	
	All β 's = -2.40	$\beta_{C-C} = -2.40$ $\beta_{C-N} = -2.57$	All β 's = -2.40	$\beta_{C-C} = -2.40$ $\beta_{C-N} = -2.57$
1	-0.08	-0.07	1.27	1.27
2	0.20	0.20	0.74	0.73
3	-0.08	-0.07	1.29	1.28
4	0.22	0.22	0.78	0.77
5	0.01	0.05	0.95	0.93
6	0.39	0.31	1.18	1.21
7	0.14	0.15	0.71	0.71
8	-0.01	-0.02	1.34	1.35
9	0.21	0.22	0.75	0.75
$\langle S^2 \rangle =$			0.796	0.774

All values after annihilation

PART II

Computation of Simple Potential Energy Surfaces

Introduction The thermal conversion of 1,2-dioxetanes to their corresponding substituted aldehydes or ketones is a reaction which is accompanied by chemiluminescence. The recent work of Turro and coworkers (1) indicates, however, that in the case of tetramethyl-1,2-dioxetane a large yield of triplet acetone is observed in the thermal decomposition and that chemiluminescence is a minor process. The mechanism of this non-adiabatic generation of triplet species from a thermal reaction of a filled shell molecule is not known and therefore we have entered into theoretical calculations to see if they could be of some aid in an analysis of this problem.

METHOD OF CALCULATION A longer range object of the work reported here is to perfect on all valence electron SCFMO-CI approach to estimating the potential energy "surfaces" of the ground and excited states (singlet-triplet) of species involved in photochemical reactions. The CNDO/2 method was chosen as a starting point (2) to generate the orbitals required for a configuration interaction estimate of the energies of the ground and excited singlet and triplet states at a particular geometrical configuration.

The major failure of the CNDO/2 method (non-CI) in reproducing the overall thermodynamics in the dioxetane decomposition was demonstrated by Kearns and coworkers (3) who showed

that the reaction is computed to be highly endothermic rather than highly exothermic (4). Although some success has been claimed for CNDO/2 (5) or the related PCILO (6) and MINDO (7) methods in predicting the relative energies of tautomers or geometrical isomers these techniques have yielded poor results in the case of small ring compounds. The unreparameterized CNDO/2 predicts (8) that cyclobutane is more stable than 2 ethylenes by 360 kcal/mole whereas the reaction is endothermic by only 18.7 kcal (9). We also found that the unaltered CNDO/2 method predicts an endothermicity of 317 kcal for the 1,2-dioxetane to 2 formaldehydes reaction whereas the estimated value is 55 kcal exothermic (4). Likewise, the PCILO method, as usually applied (6,10), is subject to the same parameterization as the parent CNDO method and predicts endothermicities of 332, 317, and 326 for the cyclobutane, oxetane, and 1,2-dioxetane breakup, respectively, grossly in contrast to reality (6,9). Errors of this magnitude can not be corrected by a simple readjustment of resonance parameters or imposition of techniques which introduce correlation terms, e.g., configuration interaction. It is obvious that some reparameterization of either the core-core repulsion or core-electron (penetration) attraction terms must be imposed. The MINDO method (11) chooses the former route by selecting a core-core term which precludes the proper imposition of configuration interaction while at

the same time being theoretically wrong. Fisher and Kollmar installed (8) as one of their features of a reparameterization of the CNDO/2 method an unclear formula for the estimation of the penetration term, V_{ab} , which states that the interaction energy of an electron at core a with nucleus b goes to infinity at infinite distance. This is theoretically in error in this limiting case and therefore unsatisfactory for a calculation of potential surface in which the reacting parts recede to infinity. In the CNDO/2 method (2) $V_{ab} = Z_b G_{ab}$, where Z_b is the core charge for nucleus b and G_{ab} is the two centered electron-electron repulsion integral. We have chosen the simple expedient of replacing V_{ab} (12) by the term $V_{ab}F$, where F is a scaling factor. In the normal CNDO/2 method $F = 1$. A change of F to 0.991 yielded a computed exothermicity of about 90 kcal instead of an endothermicity of 360 for the 1,2-dioxetane breakup. Since the V_{ab} term in CNDO/2 calculations was originally an approximation we feel that this minor parameter variation casts doubts on any claims of uniqueness of any semi-empirical parameter scheme. This parameterization merely allows one to calibrate the end points of a particular potential energy surface calculation. We otherwise retained the parameterization of the original CNDO/2 method although well realizing that the prediction of either the excited state energies or the magnitudes of energies of transition states would be in error. The hope is that the calculations will reflect the topological features of what might occur in reality.

As with a number of calculations of potential energy surfaces the dioxetane-formaldehyde computation requires the imposition of configuration interaction at the doubly as well as the singly excited level. This is easily shown by an orbital symmetry analysis similar to the classic cyclobutane-ethylene conversion (13) with the additional complication that "non-bonding" orbitals are involved. In the case presented here the geometry of the 1,2-dioxetane to 2 formaldehydes reaction was maintained in the C_{2v} point group and all distortions were done by i) stretching the O-O and C-C bonds symmetrically to yield a concerted bond breaking; ii) stretching the O-O bond while maintaining a constant C-C bond while moving the hydrogen atom pairs towards one another; and iii) stretching or compressing the C-C bond after the O-O bond stretch had reached 2.54 Å.

Table 1 lists the conventions used for the orbitals as well as a symmetry correlation between the monomer states in formaldehyde and the 1,2-dioxetane or formaldehyde dimer states. On weak interaction the 1B_2 (π - π^*) excited state of formaldehyde will split into nearly degenerate 1A_1 and 1B_2 states whereas the 1A_2 (n - π^*) monomer state will split into 1A_2 dimer states.

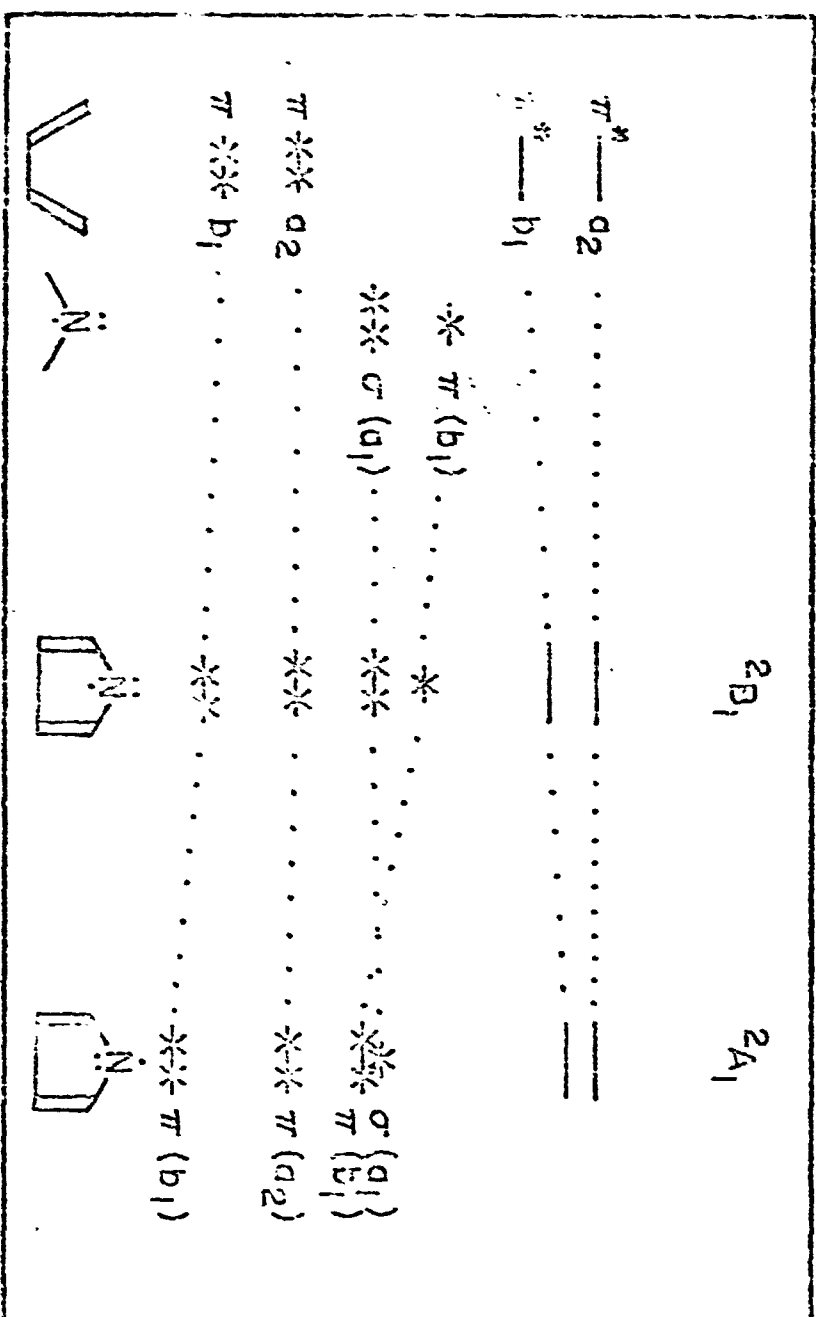
In the calculations presented here the CI treatment was limited to a total of 50 configuration of the single, double, and triple promotions of electrons from bonding to non-bonding orbitals

having symmetry characteristics belonging to each of the four irreducible representations of the C_{2v} point group. Calculations were initiated for a configuration of 1,2-dioxetane having the following bond distances and angles: C-C (1.55 Å); O-O (1.48); C-O (1.43); C-H (1.09); and H-C-H (110°).

RESULTS AND DISCUSSION: Figure 1 shows 3 different curves. Curve 1 represents the concerted breaking of the C-C and O-O bonds. Curve 2 represents the initial "breaking" of the O-O bond to a point (2.54 Å) where the C-C-O bond angle has expanded from 90° to 110° . Curve 3 represents the compression-stretching of the C-C bond after the C-C-O angle is 110° . Thus Curve 2 represents the evolution of the molecule to a more nearly singlet biradical configuration and Curve 3 represents the effect of C-C bond stretch on this "biradical".

Figure 1 shows clearly that the predicted activation energy through the biradical is much lower than in the concerted reaction. Preliminary calculations also indicate that after the O-O bond had reached the biradical configuration, twisting around the C-C bond from the cisoid (C_{2v}) to the transoid (C_{2h}) orientation is a path to lower energies. Thus, the best minimum energy path may actually represent a simultaneous O-O break and C-C twist. Curve 3 indicates that the biradical

ORBITAL ENERGIES



ORBITAL CORRELATION DIAGRAM OF BUTADIENE AND AMINO TO PYRROL

may have kinetic existence, however, in that additional energy is required to allow for a breakup to the formaldehydes.

Computationally some minor difficulties were encountered in getting SCF convergence at certain geometries, especially in the region where the amount of CI mixing in the ground state was greatest. In such regions the relative symmetries of the excited singlet states were also undergoing change. This is to be expected from a simple orbital analysis. In the biradical configuration the lowest singlet excited state was only about 2 eV above the ground state. Because of the complexity of Figure 1, we have not included the excited state behavior. This has been done in Figure 2 where we have shown a calculation of the approach of two planar formaldehyde molecules to produce a dimer at short 0-0 distances, which is a distorted form of the dioxetane. In the region of the geometry of the transition state of ground state there is a reordering of the symmetries of the excited states.

The prediction that the lowest 1B_1 and 1A_2 states in the dimer should become degenerate and evolve towards the lowest 1A_2 n- π^* state is fulfilled in Figure 2. Interestingly the lowest 1B_2 and 1A_1 excited states have not become degenerate at 3A. Examination of the 1A_1 excited state shows that it is a mixture of various doubly excited states of the π^2 to π^{*2} and n^2 to π^{*2} type. Conceptually, this state could arise from the

annihilation of two $n\text{-}\pi^*$ triplet formaldehydes and is so correlated in Figure 2 with a state designated as $^1A_1^T$. The wavefunction of the $^1A_1^T$ is an antisymmetrized product of two monocexcited functions, one for each of the monomers under the conditions that this final function must be a singlet.

The possibility that a biradical intermediate exists in the dioxetane reaction has been argued thermodynamically by O'Neal and Richardson (5). The situation is much the same as with the cyclobutane reaction as has been discussed theoretically by Salem (14) and Hoffmann (15). The possibility that such a singlet biradical has kinetic existence in the dioxetane surface raises the possibility that the triplet surface might lie at lower energies. Thus the route to the generation of triplet species in the dioxetane reactions (1) might be through a mechanism involving intersystem crossing from the singlet to the triplet biradical. We will soon perform the CI calculation on the triplet surface. However, in view of recent work on the dewar benzene to benzene conversion (16) it may well be that the hypothesis proposed above for the dioxetane reaction is a bit too convenient and that mechanisms of chemelectronic processes (1,16) are not analyzable within the context of potential surfaces based on the Born-Oppenheimer approximation of the total separation of triplet and singlet "states".

Table 1
Symmetry Designations in Dioxetane and Formaldehyde (C_{2v})
and
Correlations of Their Respective Excited States

Orbital Designations		Formaldehyde States	Dioxetane or H ₂ O Dimer States
H ₂ CO	$\begin{array}{c} \text{O}-\text{O} \\ \quad \\ \text{H}_2\text{C}-\text{CH}_2 \end{array}$		
Bond Type	Sym.	Bond Type	Sym.
σ_s	a ₁	$\sigma_{\text{C}-\text{C}}$	a ₁ , b ₂
*	a ₂	$\sigma_{\text{C}-\text{O}}$	a ₁ , b ₂
σ_a	b ₁	$\sigma_{\text{O}-\text{O}}$	a ₁ , b ₂
π	b ₂	$\sigma_{\text{C}-\text{H}}$	a ₁ , b ₁ , a ₂
		A ₁ →	A ₁ , B ₂
		A ₂ →	A ₂ , B ₁
		B ₁ →	B ₁ , A ₂
		B ₂ →	A ₁ , B ₂

* Not represented in H₂CO; σ_s = symmetric, σ_a = antisymmetric sigma bonds.

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Figure Captions

Figure 1 Energy-Geometry Behavior (After CI) of the Ground State of 1,2-Dioxetane. Curve 1 - Concerted Breaking of the O-O and C-C Bonds. Curve 2 - Breaking of the O-O Bond With C-C Held Constant. Curve 3 - Compression-Stretching of C-C Bond after O-O Bond has reached the 2.54 Å point in Curve 2. Computed Points given by large circles. Zero energy = - 1400 ev.

Figure 2 Energy-Geometry Behavior (After CI) of the Ground and Excited Singlet States of Formaldehyde Dimer.

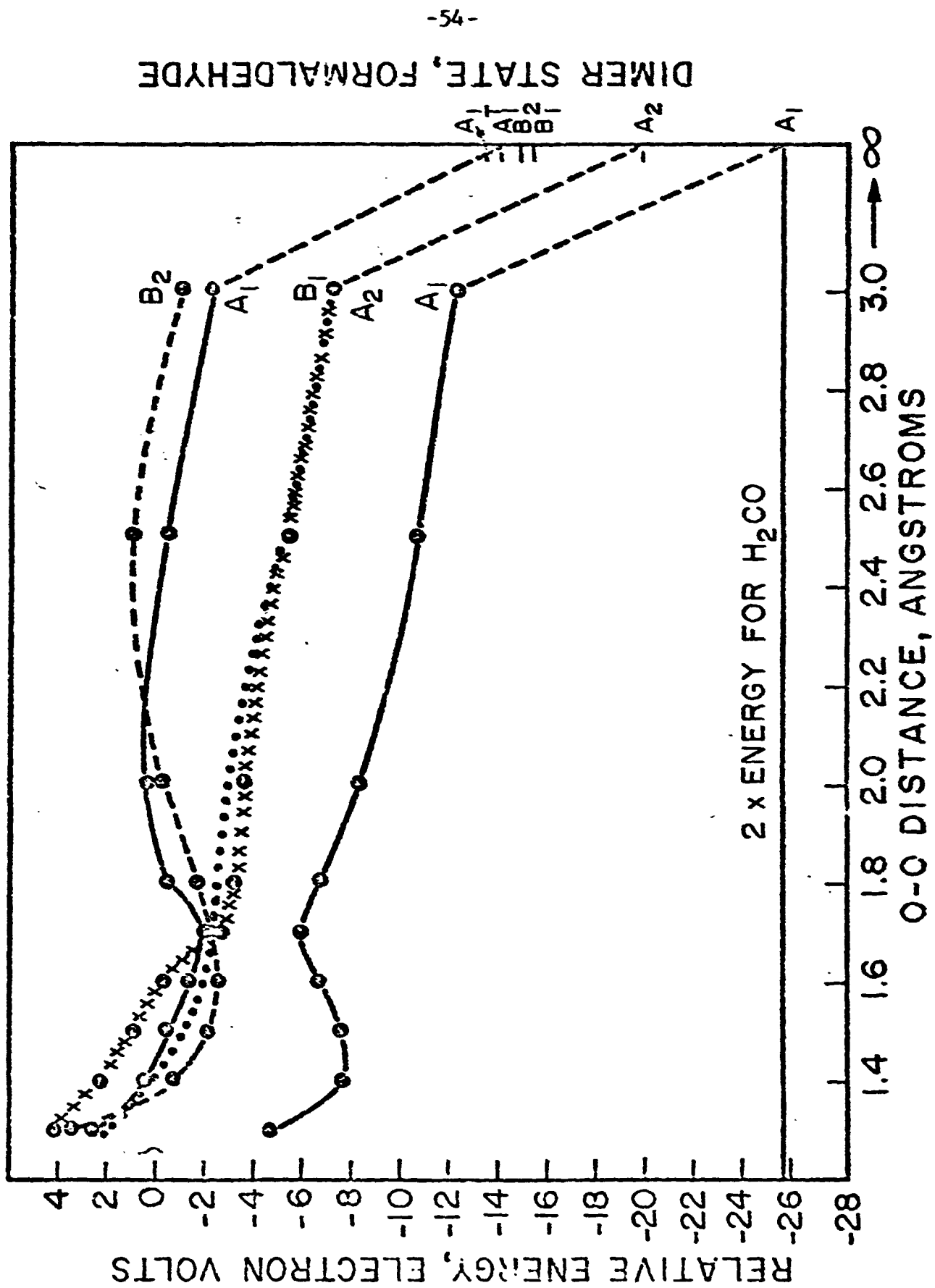
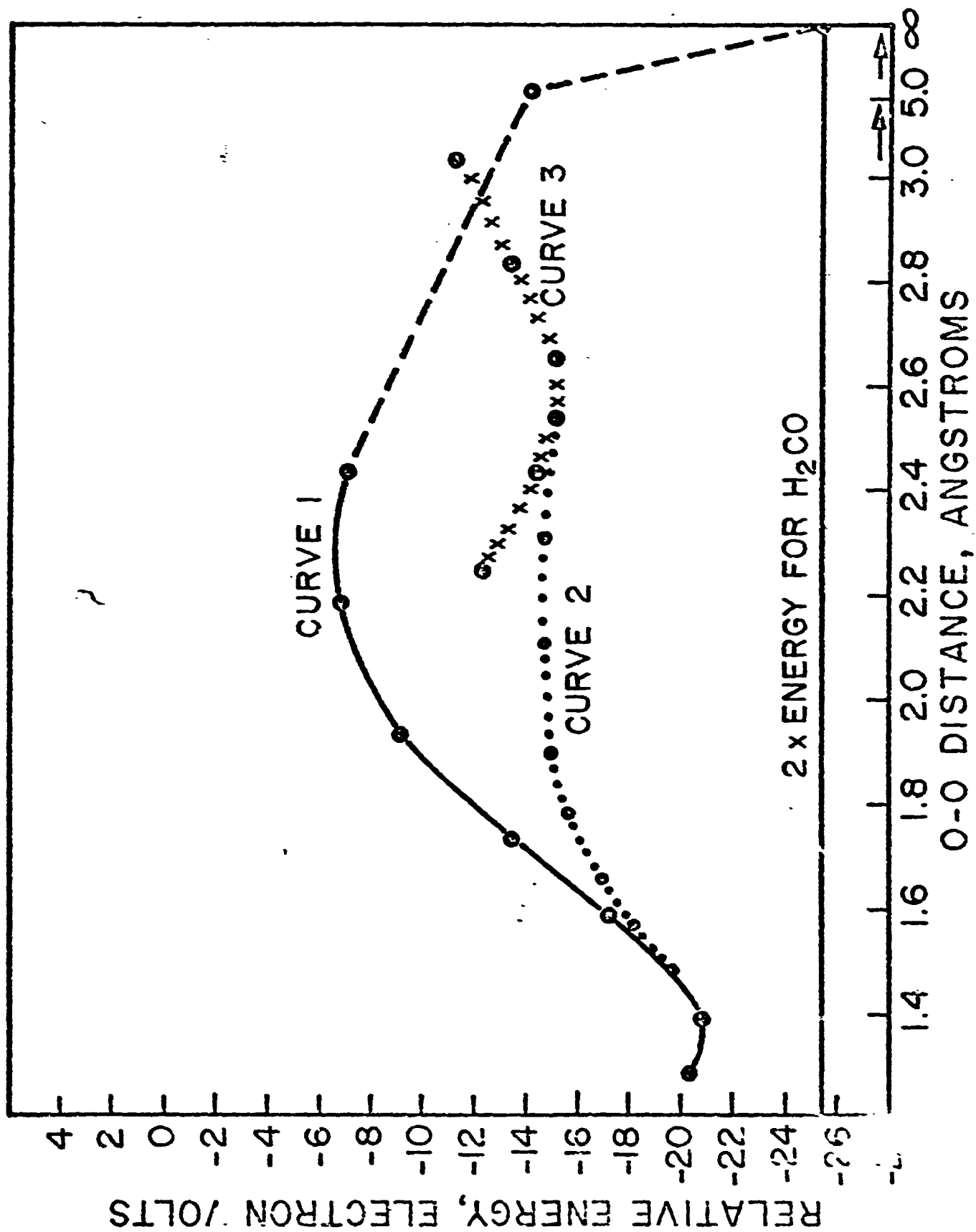


Figure 2



Part III

Photophysical Properties of Indolizine and Related Heterocycles

Last year's report contained an extensive discussion of the photophysical properties of indolizine and related azaindolizine heterocyclics. Here we will complete only that report by presenting some of the figures not previously shown. A short discussion will be presented on the significance of each figure.

Figure 4 Absorption-Fluorescence Spectra of Indole (Hexane)

The item of note here is that in the absorption spectrum there is a number of bands indicating vibrational fine structure. A detailed analysis¹ of this band system shows that there are at least two absorption bands in indole in the 35-40 kK region. The first one is concentrated in the 35-36 kK region with the second band in the 37-40 kK region. The first band is commonly referred to as the L_b transition, the second, the L_a transition. This is based on the false use of the Platt nomenclature³. Fluorescence almost always occurs from the lowest singlet and the overlap of the o-o transitions is readily seen at about 35 kK. In other solvents the picture is more complex and there is some question as to what exactly is the emitting state in hydrogen bonding solvents^{3,4}.

Figure 5 Absorption-Fluorescence Spectra of Indolizine (Hexane)

Indolizine (Figure 5 gives structure) is isomeric to indole. However, the two nearly degenerate transition in indole are strongly split in indolizine with the o-o transitions in the 26 kK region for the first transition and in the 34 kK region for the second.

Figure 6 Absorption-Fluorescence Spectra of Indolizine (Methanol)

The significance of this spectrum is that the "fine" structure of the first absorption and emission band is essentially gone, although

not nearly so much as in the case of the emission of indole in methanol. The second transition of indolizine still appears to have a fair amount of structure. It would appear that both the ground and excited states have some degree of solvent association since there is a great diminution of fine structure.

Figure 7 Absorption-Fluorescence Spectra of 2-Azaindolizine
(Hexane and Methanol)

Here in the absorption band (hexane) there is still the big split between the first and second singlet. The o-o band overlap is still seen. In methanol the smearing out of the fine structure occurs indicating that ground state complex and excited state complex formation occurs.

Figure 8 Fluorescence Spectra of 1-Azaindolizine (Hexane and Methanol)

In the absorption spectrum in hexane the separation between the first and second singlet is less than in the case of the other two indolizines; there is a strong overlap between the second and first singlet-singlet absorption bands. The overlap of the o-o band is still seen. In methanol the smearing out of fine structure is still seen.

Figure 9 Fluorescence-Absorption Spectra of 1,8-Diazaindolizine
(Hexane and Arunanol)

The commentary given above also applies to this compound.

Figure 10 Absorption-Fluorescence Spectrum of 1-Azaindolizine
in Hexane as a Function of Added Small Amounts of n-
Butanol

Here can be seen that small amounts of n-butanol (1-3% vol.) have a great effect on the absorption spectrum but little effect on the emission spectrum (virtually superimposable). This indicates

that there is specific complex formation in the ground state of 1-azaindolizine with n-butanol. In the excited state, on these butanol concentrations, there is no complex stability. We have already shown in a previous report that the excited state pK_a 's of the azaindolizines are much lower in the excited state than in the ground state. The obvious formation of exciplexes in pure methanol for the azindolizines may, therefore, not necessarily indicate hydrogen bonded complexes.

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PART IV

A Final Review of the Accomplishments of Research Done Under This Grant

A. Geometrical Influences on Non-Radiative Processes in Organic Molecules

1. Generalized Rules

The basic theoretical framework for the work carried out under the area of geometrical influences on non-radiative processes in organic molecules was done in the first year (July, 1969) of the grant and subsequently published in the open literature¹. Major photochemical reaction mechanisms were divided into four categories and each analyzed separately. This work is the basis for theoretical work still being carried out. Details of the generalized rules are reported in the first year's progress report.

2. Theoretical Calculations

a. Cis-trans isomerization. The first year's report describes calculations using a modified Pariers-Parr Pople SCF-CI estimation of the ground and excited state of a number of substituted olefins. Success was obtained in these calculations in that an analysis of the biradical verses zwitterionic mechanism could be obtained. This work has been published in the open literature².

b. Bond-breaking modes in the dioxetane decomposition. The reader is referred to another section of this year's report. A paper on this subject has been accepted for publication³.

3. Experimental Work

a. Arenediazonium photochemistry and photophysics.

Coverage of the work performed under this subject is detailed in the First and Second years' report (July 1969, July 1970). A partial report has been rendered to the open literature⁴. The first

year's report detailed some quantum yield measurements on sterically hindered arenediazonium cations and the effect of external reagents on these yields. The second year dealt with additional quantum yield measurements as well as some fluorescence quenching data. The work done on these materials is in no way yet completed.

The interest in arenediazonium photochemistry results from the fact that the reaction is fairly exothermic. Thus it belongs to a class of materials in which either the possibility of chemiluminescence exists or that the photoproducts might be left in their excited states yielding prompt luminescence, a rare phenomena. The work under the grant shows that none of these features exist. However, the materials are strange in that even at extremely low temperature, when photochemistry does not apparently occur, luminescence does not occur. The photoreactions are extremely fast, estimated by us to be in the picosecond region. An analysis of the theoretical aspects of this problem is still occurring but it now appears that the arene cation (analyzed by us theoretically and in the open literature⁵) might very well have a triplet ground state. This produces gross complexities in the ground and excited state potential energy surfaces for arenediazonium cations in that crossing can occur. An additional grant proposal covering this subject has been submitted to N.S.F.

b. Photoprocesses in Indolizine and Azaindolizine. This area was covered in the third (July 1971) and fourth (June 1972) year (this report) and has been reported in the open literature⁶. The major feature in this class of molecules is that their fluorescence lifetimes is coupled with high yields of emission and little phosphorescence. These features indicate that the molecules

undergo little intersystem crossing. Why this is so has only been analyzed within the context that either an insufficient number of triplets occur below the lowest singlet or that there is a poor misplacing of these levels. The problem still requires the measurement of triplet-triplet spectra to obtain the position of these triplets. In any case, the discovery of these unusual photophysical effects plays an important role in the theory of non-radiative processes and effects of geometry on these processes.

c. Stabilities of Nitrogen Containing Heterocyclic Radicals.

This part of the research was devoted to attempting to experimentally detect radicals of the type R-N-R and to attempt to rationalize, theoretically, their electronic structures. The experimental work, detailed in the second year's report was entirely without success and even to this date no radicals of the pyrrolyl type (unsubstituted) have been reported in the literature.

The theoretical analysis of this problem is reported in this year's report which is a partial repetition of that submitted in the second year's report. A paper has been submitted for publication to the J. Am. Chem. Soc.

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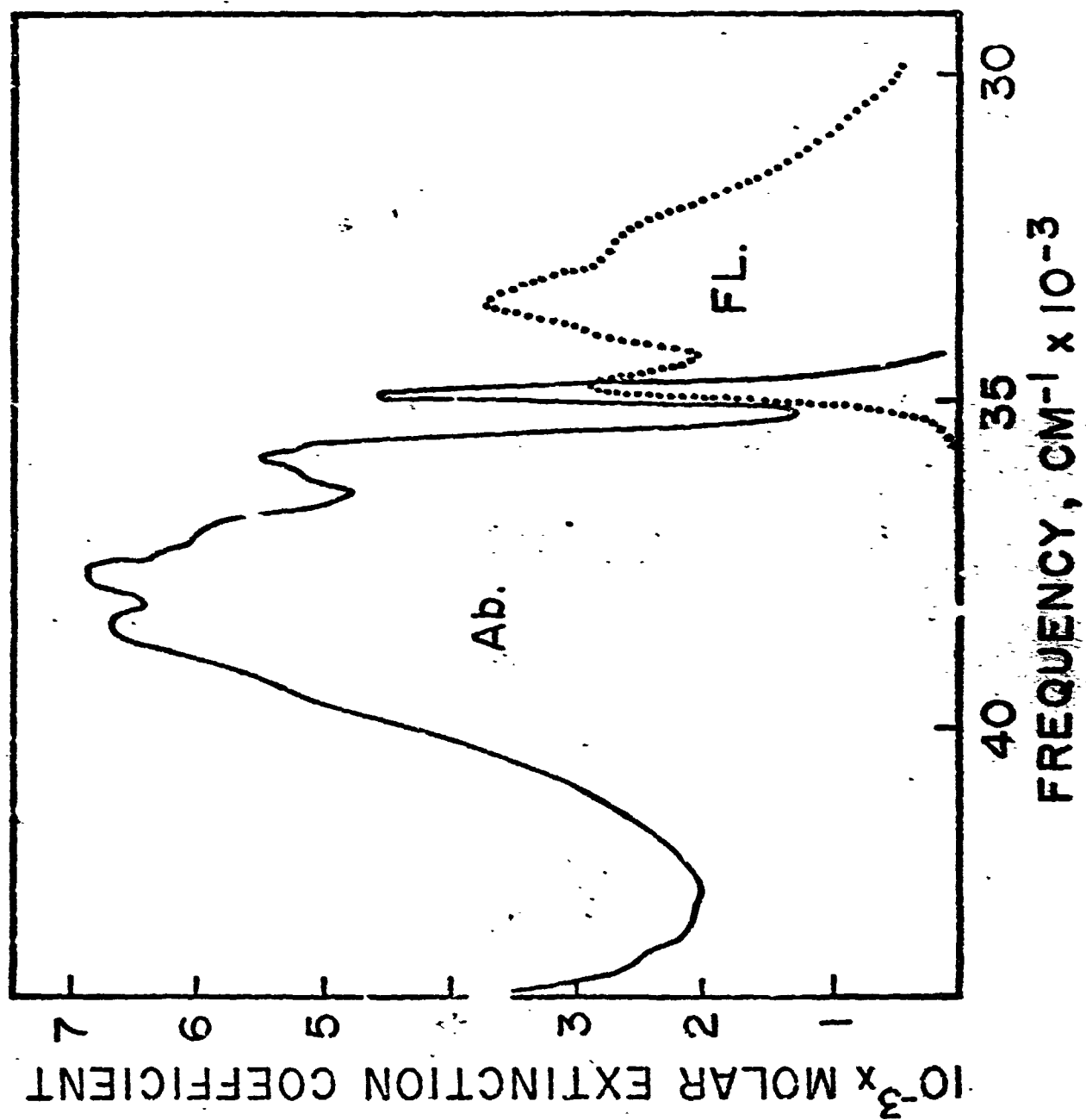


Figure 4

INDOLE

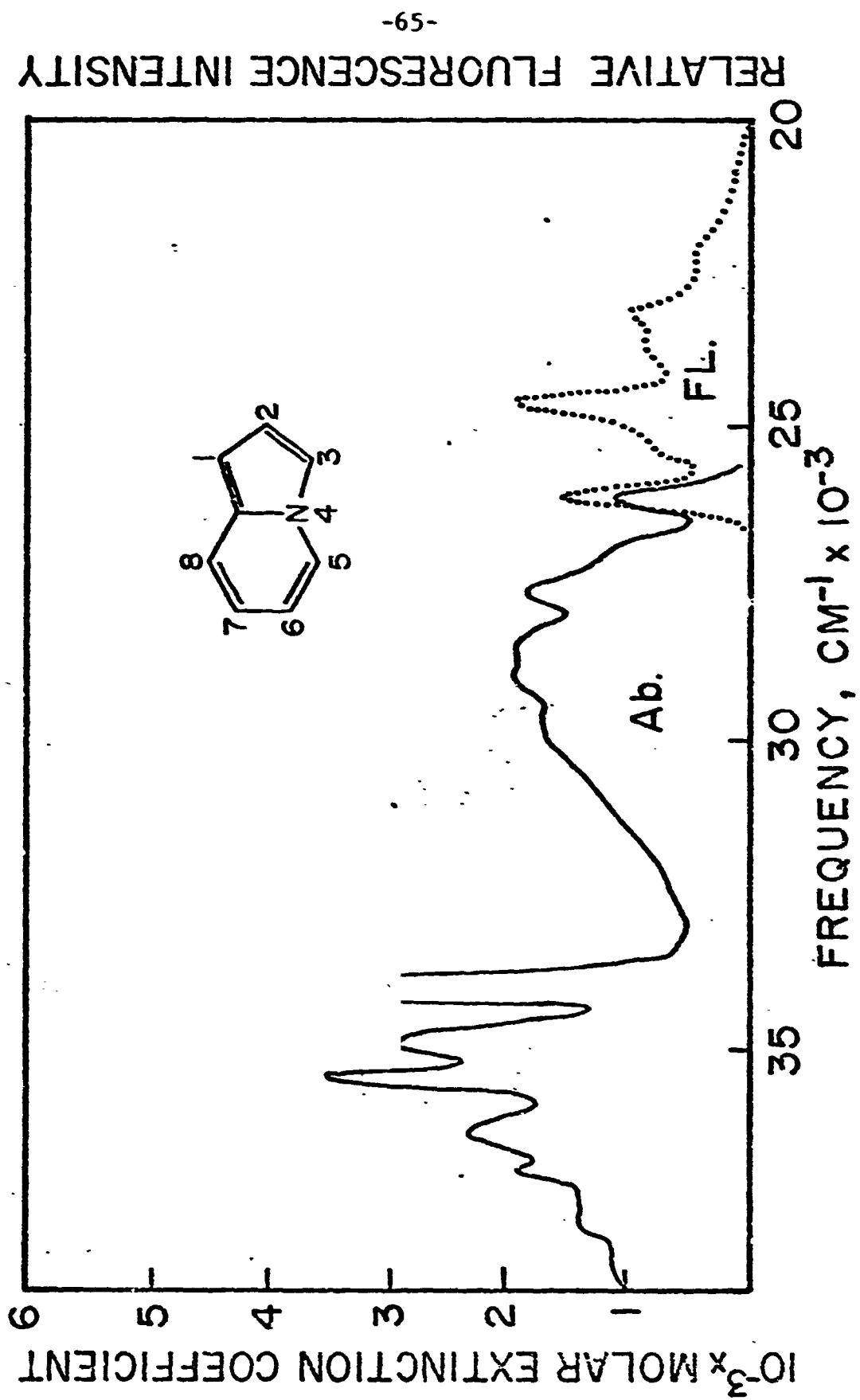


Figure 5

INDOLINE

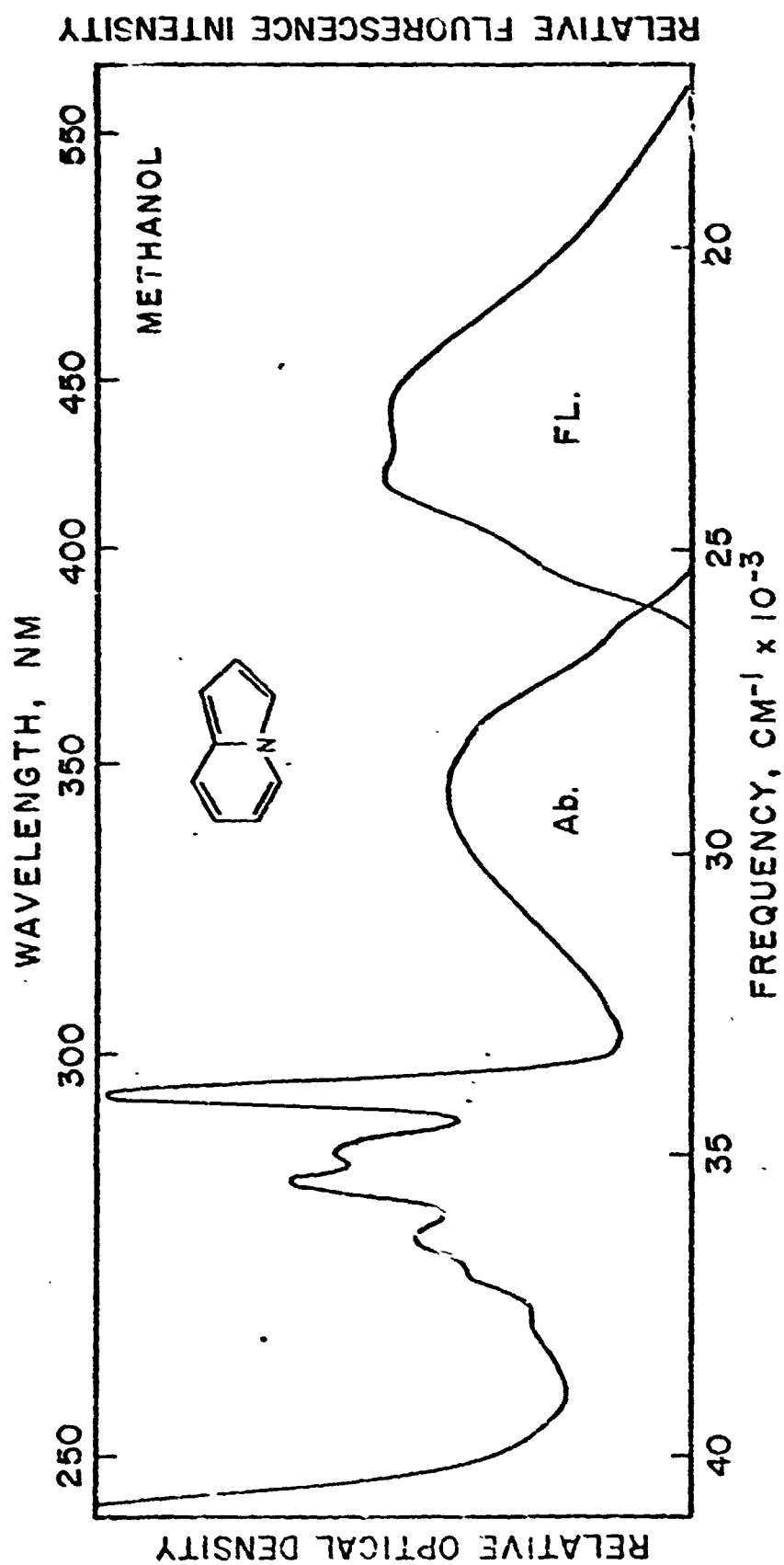


Figure 6
INDOLINE

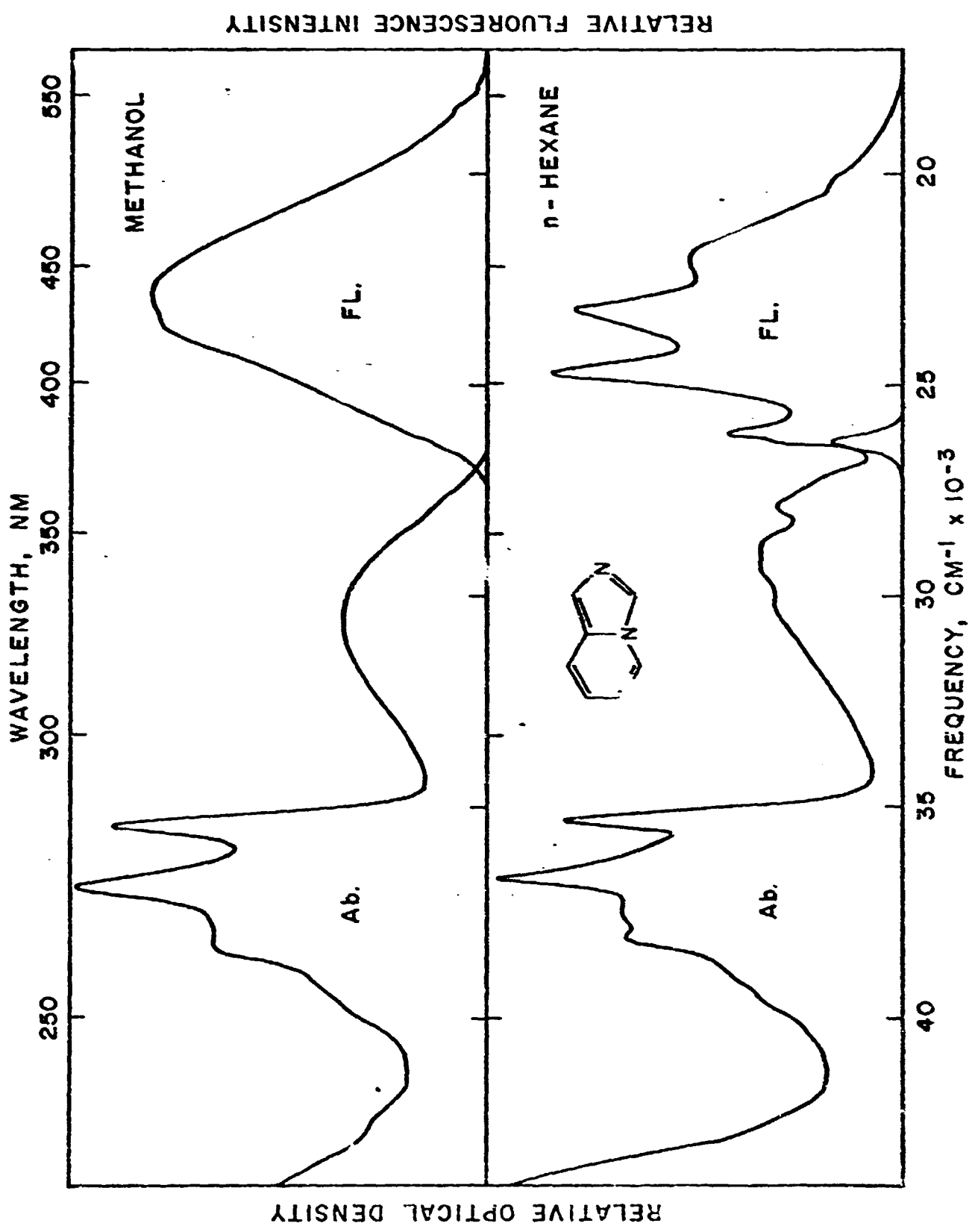


Figure 7

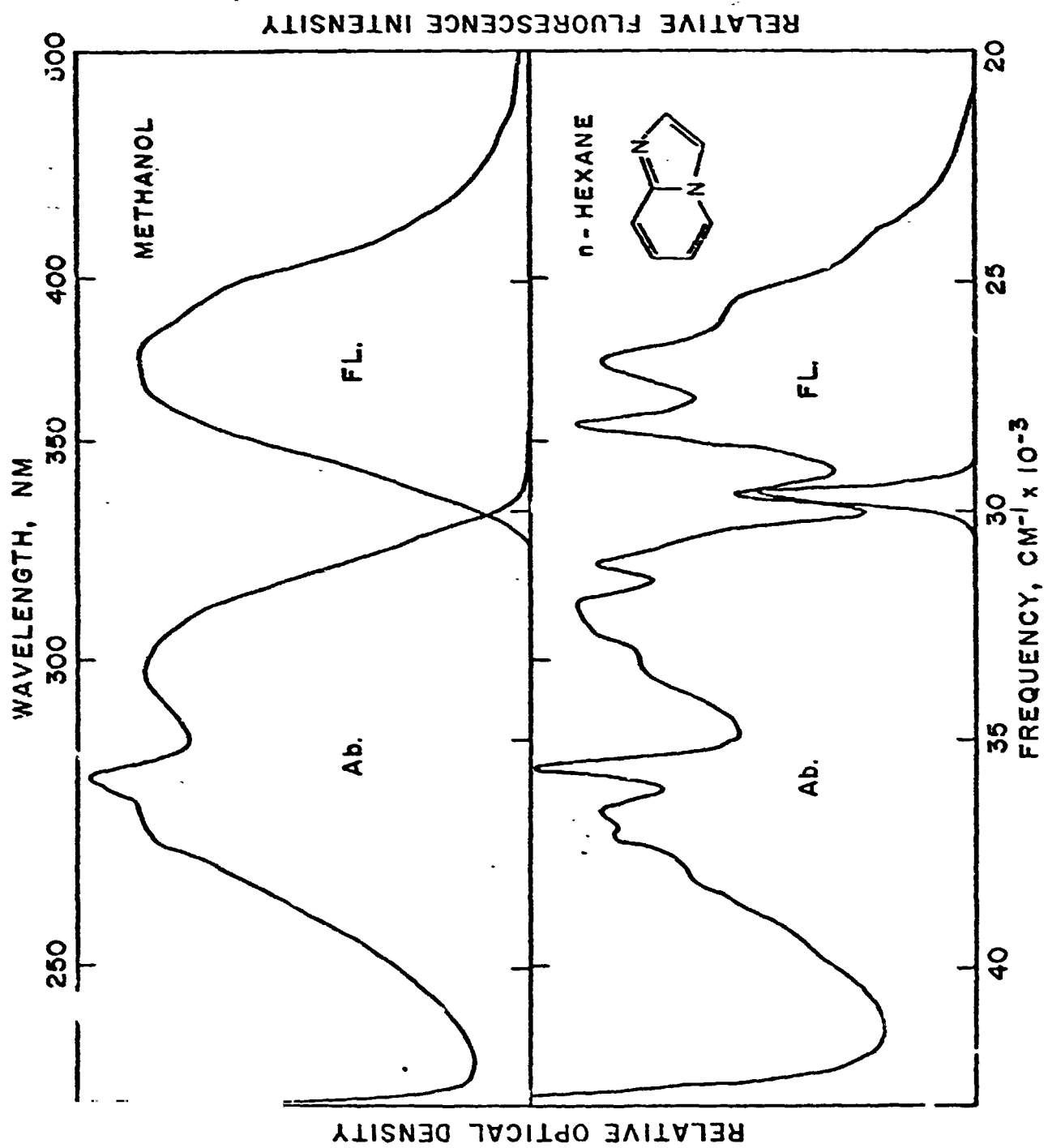


Figure 8

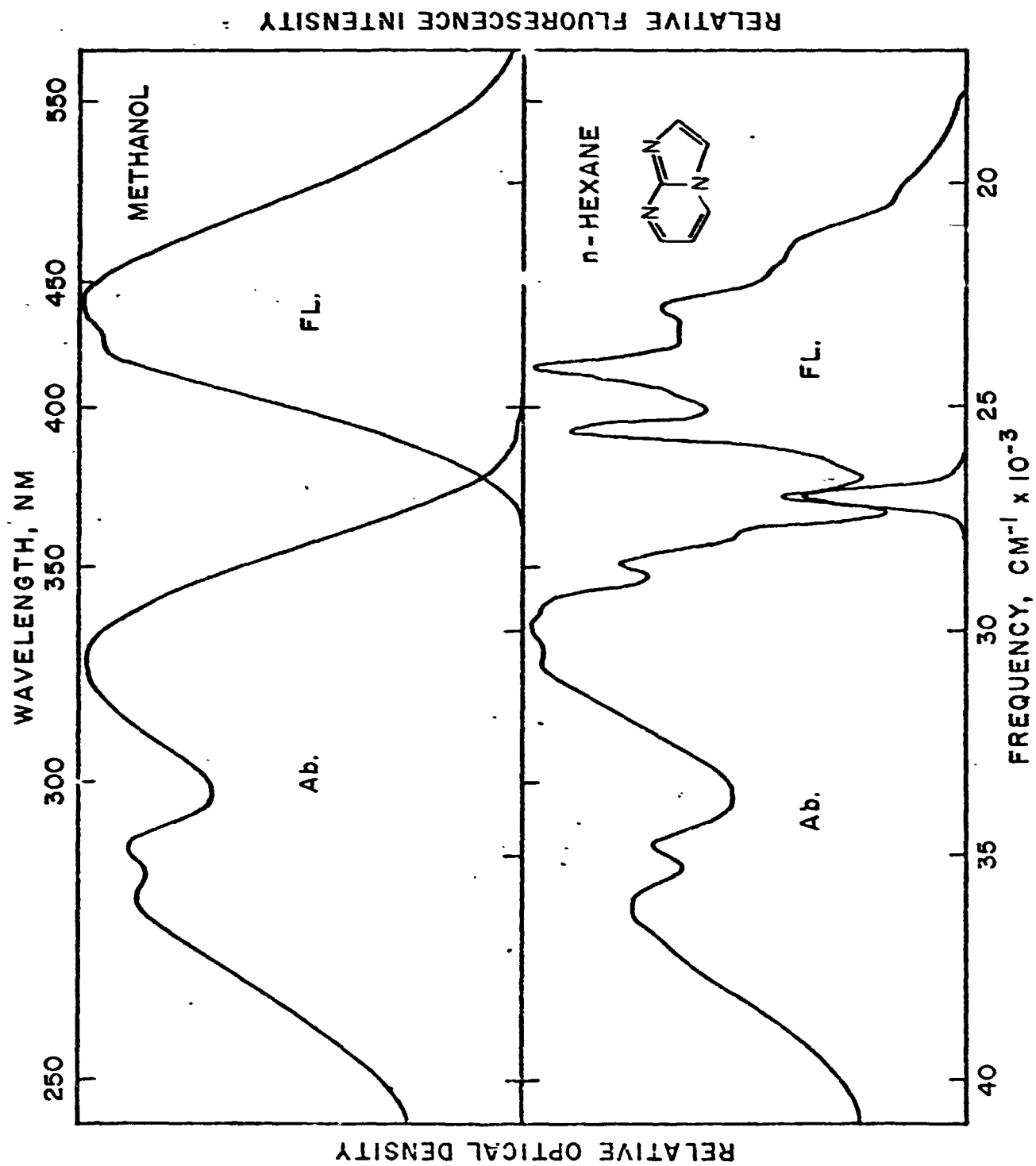


Figure 9

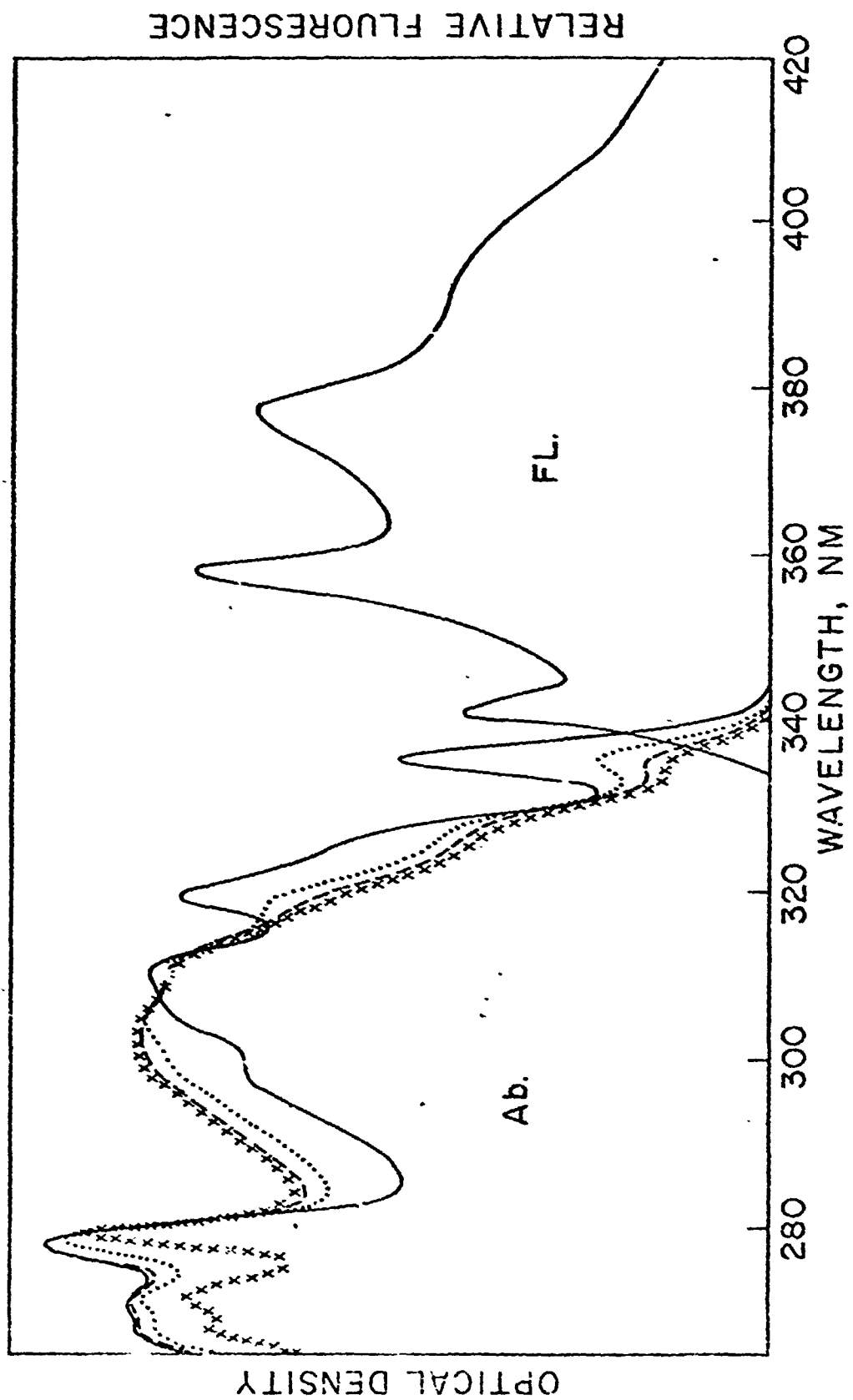


Figure 10